(12) UK Patent Application (19) GB (11) 2 207 545 (13) A

(43) Application published 1 Feb 1989

(21) Application No 8717859

(22) Date of filing 28 Jul 1987

(71) Applicant
Lillwyte Societe Anonyme
(Incorporated in Luxembourg)
2 Rue des Girondins, Luxembourg

(72) Inventors
Walter George Budgen
Peter Raymond Smith

(74) Agent and/or Address for Service
Kilburn & Strode
30 John Street, London, WC1N 2DD

(51) INT CL[4]
H01M 2/08 10/39

(52) Domestic classification (Edition J):
H1B 1039 208

(56) Documents cited
GB A 2035995 US 4341849 US 4291107

(58) Field of search
H1B
Selected US specifications from IPC sub-class H01M

(54) Glass seal for sodium-sulphur cells

(57) The invention provides a method of sealing an alpha-alumina component to a beta-alumina component in an electrochemical cell, using a high-borate borosilicate glass. The glass comprises 10-25% by mass B_2O_3 and 65-75% siO_2, with the major proportion by mass of the balance being Al_2O_3 and alkali metal oxide, and the glass comprising at most 1% by mass alkaline earth metal oxides. The invention also provides a hermetic seal of said glass between an alpha-alumina component and a beta-alumina component in an electrochemical cell; and such cell which incorporates said seal.

GB 2 207 545 A

2207545

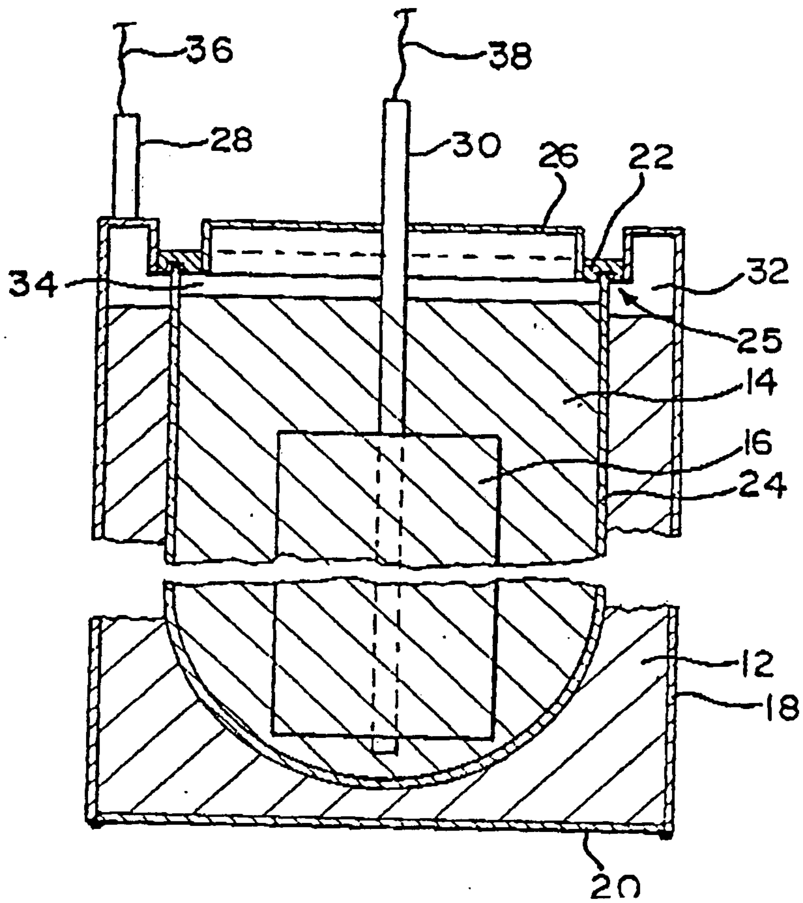

FIG 1

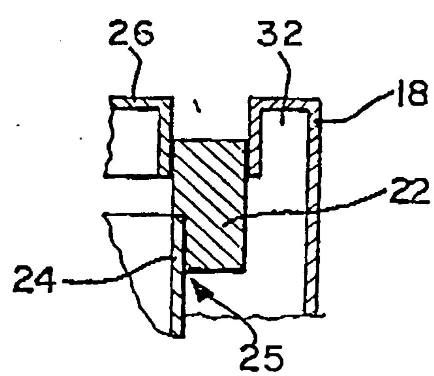

FIG 2

2207545

"ELECTROCHEMICAL CELL"

THIS INVENTION relates to an electrochemical cell. More particularly the invention relates to the sealing of alpha-alumina to beta-alumina in an electrochemical cell.

According to the invention there is provided a method of sealing an alpha-alumina component to a beta-alumina component in an electrochemical cell, which method comprises using a high-borate borosilicate glass to seal the alpha-alumina component to the beta-alumina component, the glass comprising 10- 25% by mass B_2O_3 and 65%- 75% by mass SiO_2, the major proportion by mass of the balance comprising Al_2O_3 and alkali metal oxide, and the glass comprising at most 1% by mass alkaline earth metal oxides.

The B_2O_3 content of the glass is preferably 12-20% by mass, more preferably 14-17% by mass. The SiO_2 content in turn is preferably 66-73% by mass, more preferably 67-70% by mass. The glass may comprise 3-8% by mass Al_2O_3, preferably 5-7% by mass. The alkali metal oxide may be essentially Na_2O, and may form 5-10% by mass of the glass, preferably 7-8% by mass. The alkaline earth metal oxide content of the glass is

preferably less than 0,5% by mass, more preferably less than 0,3% by mass. The glass may comprise 1-3% by mass ZnO.

The Applicant has found that a suitable glass for use in the method of the present invention is a high-borate borosilicate glass available under the trade mark SCHOTT from Schott Glaswerke, Mainz, Germany, as Type No. 8245. This glass has the following composition on a mass basis, as determined by X-ray fluorescence:

Constituent	Proportion By Mass (%)
B_2O_3	15,6
SiO_2	69,8
Al_2O_3	5,4
BaO	less than 0,1
CaO	less than 0,1
MgO	nil
K_2O	less than 0,1
ZnO	2,0
Na_2O	7,2

The invention extends to a hermetic seal between an alpha-alumina component and a beta-alumina component in an electrochemical cell, which comprises a glass as described above.

The invention extends also to an electrochemical cell which comprises an alpha-alumina component and a beta-alumina component, which components are sealed together by means of a glass as described above.

In such cell, the alpha-alumina component may be a ring of alpha-alumina, sealed to the mouth of a tube constituting the beta-alumina component, the cell having a housing sealed to the alpha-alumina ring.

The cell may have a sodium anode, and may be a sodium/sulphur cell.

Instead, it may have a sodium anode and, in its discharged state, a cathode which comprises as its active cathode material a transition metal selected from the group comprising Fe, Ni, Cr, Co, Mn and mixtures thereof, or a compound of at least one said transition metal with one or more numbers of the group comprising carbon, nitrogen, boron, silicon and phosphorous, the active cathode material being dispersed in an electrolyte-permeable electronically conductive porous cathode matrix impregnated by a sodium chloroaluminate molten salt electrolyte and having sodium chloride dispersed therein in particulate form. Such transition metal-based active cathode materials are chlorinated upon charging, to the corresponding chlorides. Thus, in the case of metallic cathode materials, the chlorides are eg $FeCl_2$, $NiCl_2$, $CrCl_2$, $CoCl_2$ or $MnCl_2$. In such cells, the housing may be of a metal which is at least as noble as the transition metal of the cathode, and this housing, and a metal closure for the mouth of the beta-alumina tube, may be sealed to the alpha-alumina component, eg by thermocompression bonding or by sealing by means of the glass described above.

The actual sealing of the alpha-alumina component to the beta-alumina component can be effected in any convenient known fashion. Thus the glass may be employed as a powder, or as a preform such as a glass ring, introduced between the respective surfaces of alpha-alumina and beta-alumina to be sealed together. In each case the glass will be fused, hermetically to seal the components together; and similar procedures may be followed to seal the alpha-alumina component to the casing and tube closure by means of glass.

The invention will now be described, by way of example, with reference to the accompanying diagrammatic drawings, in which;

Figure 1 shows a schematic sectional side elevation of an electrochemical cell according to the invention ;

Figure 2 shows a detail of the seal between the alpha-alumina ring and the beta-alumina tube of an alternative construction for the cell of Figure 1.

In the drawing, reference numeral 10 generally designates an electrochemical cell in accordance with the invention. The cell is shown broken midway along its length, typically having an outside diameter of about 30-70 mm and a length of about 200-600 mm. The cell shown has a molten sodium active anode material 12, a sodium aluminium chloride molten salt electrolyte 14 and a cathode 16 which is immersed in the electrolyte 14 and in its charged state comprises an electrolyte-permeable porous iron matrix which is electronically conductive and contains $Fe/FeCl_2$ in dispersed form therein as its active cathode substance. The matrix of the cathode 16 is saturated with the electrolyte 14 and has sufficient finely divided NaCl dispersed therein to ensure that, in all states of charge of the active cathode substance,

the electrolyte 14 is

stoichiometrically exact $NaAlCl_4$.

The cell 10 has a mild steel outer casing 18 having a base 20 for supporting it in an upright attitude as shown. The casing 18 is sealed to an annular alpha-alumina insulating ring 22. An open ended beta-alumina separator tube 24 is located concentrically within the casing 18, the lower end of the tube 24 being closed and the upper or open end of the tube 24 being glass-sealed to the alpha-alumina ring 22 in sealing fashion. In this regard it will be noted that the ring is rectangular in radial cross-section, and on its axially inner face i.e. its lower or inside face as shown in the drawing, it has a circumferential groove 25 in which the rim of the open end of the tube 24 is received, and in which said rim is sealed by means of said glass Type No. 8425. Instead, said rim may be sealed by said glass into a circumferential rebate formed along the radially inner edge of said face of the ring 22, eg by means of counterboring the ring 22, as shown in the detail of Figure 2. The open end of the tube is closed by a closure disc 26 sealed by a glass to the radially inner surface of the alpha-alumina ring 22. An anode terminal post 28 is welded to the casing 18, and a cathode terminal post 30 passes through a sealed central opening in the disc 26, downwardly into the electrolyte 14. The lower portion of the post 30 is embedded in and in electronic contact with the matrix of the cathode 16. The matrix acts as a cathode current collector, while the housing 18 acts as the anode current collector. There is a gas space 32 above the anode material 12, and a gas space 34 above the electrolyte 14. The cell is shown connected to an external circuit by electrical leads 36, 38 connected respectively to posts 28, 30.

The space between the casing 18 and tube 24, occupied by the anode sodium 12, forms an anode compartment, and the interior of the tube 24 forms a cathode compartment. These compartments are separated from each other by the separator tube 24, and by sealing of the tube 24, casing 18 and disc 26 to the alpha-alumina ring 22, the casing 18 similarly being sealed to the radially outer surface of the ring 22 by a glass.

The overall charge/discharge reaction of the cell can be represented by the reaction:

$$2Na + FeCl_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 2NaCl + Fe$$

Accordingly, sodium passes from the anode compartment to the cathode compartment during discharging, through the separator 24; and it passes in the opposite direction during charging.

The Applicant has found that said glass Type No. 8245 high-borate borosilicate glass provides excellent sealing of the cell, particularly of the ring 22 to the separator 24, in hermetic fashion, and is resistant to thermal shock at the operating temperature of the cell (200-350°C) and chemically resistant to the cell environment, particularly the molten sodium and the sodium aluminium chloride. Glasses that resist corrosion by molten sodium do not necessarily withstand sodium aluminium chloride.

CLAIMS

1. A method of sealing an alpha-alumina component to a beta-alumina component in an electrochemical cell, which method comprises using a high-borate borosilicate glass to seal the alpha-alumina component to the beta-alumina component, the glass comprising 10- 25% by mass B_2O_3 and 65%- 75% by mass SiO_2, the major proportion by mass of the balance comprising Al_2O_3 and alkali metal oxide, and the glass comprising at most 1% by mass alkaline earth metal oxides.

2. A method as claimed in claim 1, in which the B_2O_3 content of the glass is 12 - 20% by mass, the SiO_2 content of the glass is 66-73% by mass, the Al_2O_3 content of the glass is 3-8% by mass, the alkali metal oxide in the glass is essentially Na_2O, and the alkaline earth metal content of the glass is less then 0,5% by mass.

3. A method as claimed in claim 2, in which the B_2O_3 content of the glass is 14-17% by mass, the SiO_2 content of the glass is 67-70% by mass, the Al_2O_3 content of the glass is 5-7% by mass, the Na_2O content of the glass is 5-10% by mass, and the alkaline earth metal oxide content of the glass is less than 0,3% by mass.

4. A method as claimed in claim 3, in which the glass is glass Type No. 8245 obtained from Schott Glaswerke.

5. A method of sealing an alpha-alumina component to a beta-alumina component in an electrochemical cell, substantially as described herein.

6. A hermetic seal between an alpha-alumina component and a beta-alumina component in an electrochemical cell, which seal is a high-borate borosilicate glass comprising 10-25% by mass B_2O_3 and 65-75% by mass SiO_2, the major proportion by mass of the balance comprising Al_2O_3 and alkali metal oxide, and the glass comprising at most 1% by mass alkaline earth metal oxides.

7. A seal as claimed in claim 6, in which the glass is glass Type No. 8245 obtained from Schott Glaswerke.

8. An electrochemical cell which comprises an alpha-alumina component and a beta-alumina component sealed together by means of a glass which is a high-borate borosilicate glass comprising 10-25% by mass B_2O_3 and 65-75% by mass SiO_2, the major proportion by mass of the balance comprising Al_2O_3 and alkali metal oxide, and the glass comprising at most 1% by mass alkaline earth metal oxides.

9. A cell as claimed in claim 8, in which the alpha-alumina component is a ring of alpha-alumina, and is sealed to the mouth of a tube which constitutes the beta-alumina component, the cell having a housing sealed to the alpha-alumina ring.

10. A cell as claimed in claim 9, which has a sodium anode, and, in its discharged state, a cathode which comprises as its active cathode material, a transition metal selected from the group comprising Fe, Ni, Cr, Co, Mn and mixtures of said transition metals, or compound of at least one said transition metal with one or more members of the group comprising carbon, nitrogen, boron, silicon and phosphorous.

11. An electrochemical cell substantially as described and as illustrated herein with reference to the accompanying drawing.

Published 1988 at The Patent Office, State House, 66 71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office.
[illegible] St Mary Cray, Kent. Con. 1 87.